

Molecular Dynamics Simulation of Adhesion at Epoxy Interfaces

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ABSTRACT

The effect of moisture on adhesives used in aerospace applications can be modeled with chemically specific techniques such as molecular dynamics simulation. In the present study, the surface energy and work of adhesion are calculated for epoxy surfaces and interfaces, respectively, by using molecular dynamics simulation. Modifications are made to current theory to calculate the work of adhesion at the epoxy-epoxy interface with and without water. Quantitative agreement with experimental values is obtained for the surface energy and work of adhesion at the interface without water. The work of adhesion agrees qualitatively with the experimental values for the interface with water: the magnitude is reduced 15% with respect to the value for the interface without water. A variation of 26% in the magnitude is observed depending on the water configuration at a concentration of 1.6 wt%. The methods and modifications to the method that are employed to obtain these values are expected to be applicable for other epoxy adhesives to determine the effects of moisture uptake on their work of adhesion.

INTRODUCTION

The use of adhesives to assemble aircraft structure has several advantages including reduced weight and part count. Bonded assembly and repair of composite

structures without fasteners is especially desirable, but there are concerns about long-term durability. Over the lifetime of the aircraft, the adhesives are subjected to various mechanical, thermal, and environmental conditions that affect their performance. Chemically specific analyses are required that explore the application of the adhesives under these various conditions. In this regard, molecular dynamics (MD) simulation is a potentially useful tool for understanding the effects of moisture on surfaces of polymeric materials. Clancy and Mattice [1] simulated thin films to obtain the surface energies and the work of adhesion for polyolefin interfaces. Similar MD-based methods have also been applied to polycarbonate/silane interfaces [2].

In the present work these techniques are extended to calculate the work of adhesion at epoxy interfaces with and without water. The objective is to adapt the methodology to predict values for the surface energies and work of adhesion. For this purpose, MD simulations of epoxy networks were carried out in bulk, as thin films, and with interfaces. A method is proposed to determine the work of adhesion for epoxies in the presence of water. The paper will present the details of the molecular model and the MD simulations, followed by the methods used to obtain the surface energy, work of adhesion, and work of adhesion in the presence of water. A comparison will be provided of calculated values with the experimental values available in the literature.

METHODS

Construction of the Epoxy Networks for Simulation

The molecular structure represents the epoxy as the tetraglycidyl ether of diaminodiphenylmethane (TGDDM) cross-linked with diaminodiphenylsulfone (DDS). The structures of the TGDDM and DDS monomers are given in Figure 1(a) and (b). A total of 151 TGDDM molecules and 192 DDS molecules were

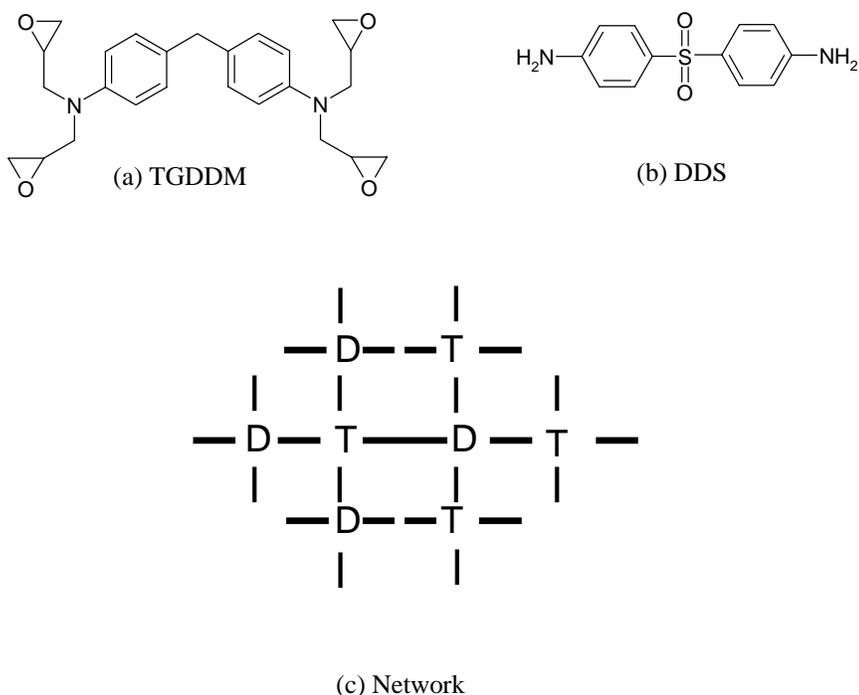


Figure 1. Molecular structures of (a) TGDDM and (b) DDS and (c) the network that is formed by crosslinking them. T=TGDDM; D=DDS.

connected as shown schematically in Figure 1(c). Only 342 out of a total of 604 possible TGDDM sites are reacted due to space-filling considerations during the structure packing. The cross-linking density is therefore 57%. The TGDDM repeat units were terminated in epoxide rings, and the DDS repeat units were terminated as amines.

The packed molecular structure shown in Figure 2(a) has 14779 atoms, and is comprised of one epoxy network in the form shown in Figure 1(c). It was developed by compressing the network in each of the three directions simultaneously at a rapid pace of 0.5% every 3000 MD time steps until the internal virial stress increased to an average of 0.1 GPa. Then the structure was expanded until an equilibrated configuration was achieved at zero stress. This equilibrated structure is representative of bulk solid TGDDM/DDS and is fully periodic in all three directions. The density of the bulk epoxy was 1.16 g/cm^3 . For comparison, density values of $1.12\text{-}1.19 \text{ g/cm}^3$ are reported for a bisphenol A type resin cured with a cyclic amine cure [3].

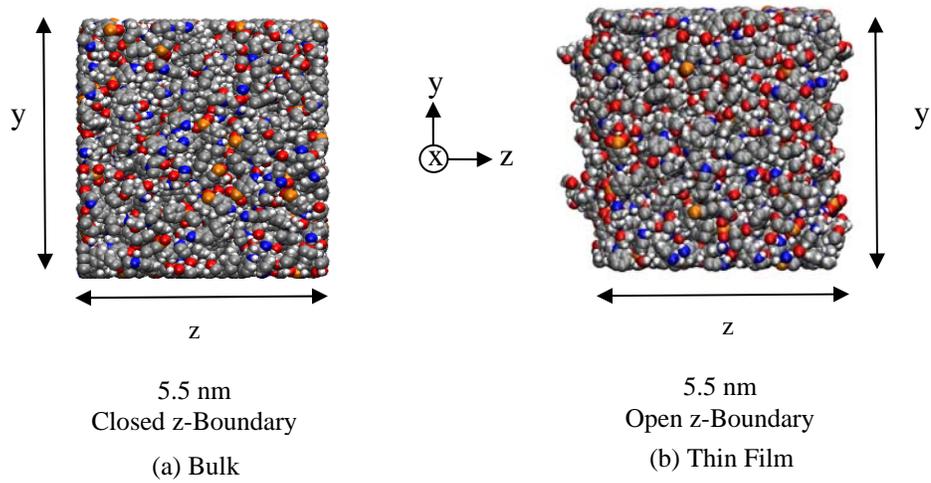


Figure 2. (a) Bulk and (b) thin film molecular structures of epoxy. Colors: C=dark grey, H=light grey; O=red; N=blue; S=orange. The x-axis goes into the page.

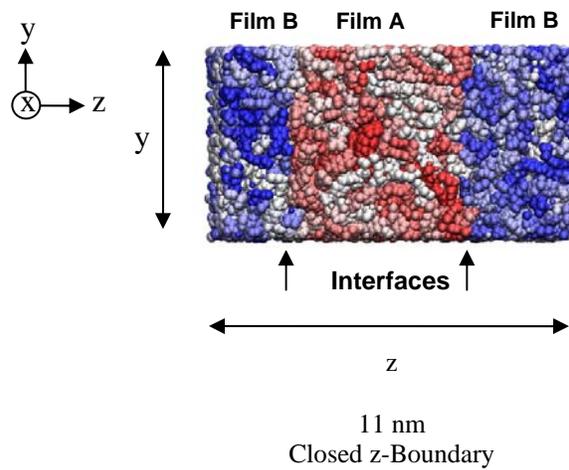


Figure 3. Epoxy-epoxy interface simulation with 2 interfaces. Film 1 is shaded red and Film 2 is shaded blue.

Molecular Dynamics Simulations

MD simulations of the epoxy network were carried out in different forms to provide input data for the surface energy and work of adhesion calculations. The network was simulated in bulk form as just described, in thin film form, with interfaces between, and with water added at the interfaces.

The thin film epoxy structure shown in Figure 2(b) is also comprised of the same network as in Figure 2(a). It was compressed in the x- and y- directions, and two walls of frozen Lennard-Jones particles were used to block the periodicity in the z-direction. This structure when replicated in the x- and y-dimensions forms a thin film rather than a bulk solid. Once an equilibrated structure at zero stress was obtained, the walls were removed, and the resulting thin film structure was equilibrated with the z-boundary open. The thickness of the film was about 5.5 nm.

The epoxy simulation with the interface shown in Figure 3 was constructed by placing two epoxy thin film networks side by side and closing the boundaries in each of the 3 directions to make the system fully periodic (closed boundary). In this simulation there are two epoxy-epoxy interfaces. The original methodology had only one epoxy-epoxy interface because the boundary normal to the film cross-section was left open so that the system was non-periodic in that direction [1]. Two simulations of the epoxy-epoxy interface were performed. The first simulation included the two epoxy films side by side. In the second simulation (not shown), the configuration of the epoxy films was modified by reversing the z-direction of the second film relative to that of the first film.

To produce the epoxy-epoxy interface with water in Figure 4(a), 196 water molecules were equally divided between the two epoxy-epoxy interfaces. This concentration is equivalent to an uptake of 1.6 wt % water per interface. In Figure 4(b), the densities of the epoxy and the water are plotted as a function of the distance along the z-direction of the epoxy with water at the interface simulation. Altogether 6 simulations were carried out, each with the water molecules starting from a different initial configuration. Each configuration was generated in two steps. The first step was to perform an initial simulation of an epoxy interface with

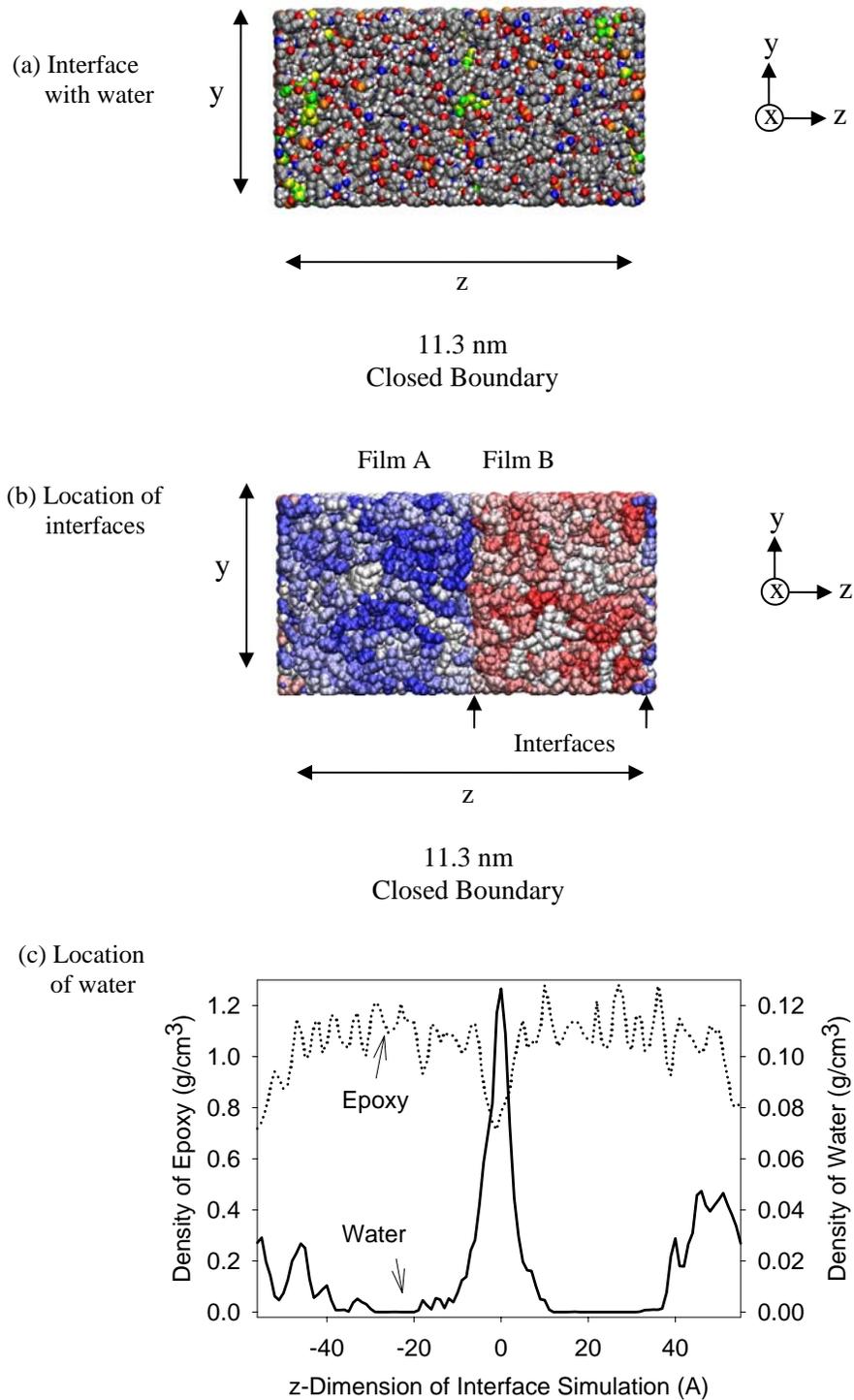


Figure 4. (a) Molecular structure of epoxy interface with water, (b) location of interfaces, and (c) location of water at interfaces along the z-direction. Colors as in Figures 2 and 3 with the water hydrogens in green and oxygens in yellow.

water simulation for 10000 steps with the z-dimension at 11.7 nm allowing for a small separation of the interfaces. At this interfacial distance the water molecules are able to assume different configurations. In the second step, the z-dimension was incrementally reduced to 11.3 nm for the production simulations.

All the simulations were carried out under NVE (constant number of atoms, volume and energy) conditions at 300 K. The electrostatic interactions were calculated out to 1.3 nm by direction summation which was sufficient to screen the electrostatic interactions without using an Ewald summation [4]. The molecular simulation package DL-POLY [5] was used to perform the simulations.

Force fields

The AMBER force field was used for the simulations[6]. Sulfur parameters for the AMBER force field were also taken from the literature [7,8]. The water is simulated as a TIP3P water molecule [9,10]. In this model, the water has 3 sites co-located with the atomic position, fixed bond lengths, and partial atomic charges at each atomic site.

Atomic charges were obtained using the RESP method in the NWCHEM program [11]. Geometries of the monomers in Figure 1 were optimized at the Hartree-Fock (HF) level using the STO-3G basis set and electrostatic potentials were calculated using HF with the 6-31G* basis set.

It was found that by reducing all Lennard-Jones epsilon parameters and calculated partial charges by 25%, the surface energy of the epoxy (to be described in the next section) was brought into quantitative agreement with experimental values. Changing Lennard-Jones and Coulombic parameters for potential refinement has precedence in the literature [12]. Therefore, the reduced parameters are used in the present calculations.

Surface energy

To determine the surface energy of the epoxy, two MD simulations are required. The first simulation is of the bulk epoxy packed with periodicity in all three

dimensions. The second simulation is of the epoxy in thin film form. The surface energy γ is then determined from the difference in the potential energies E_{bulk} and E_{film} :

$$\gamma = (E_{film} - E_{bulk}) / 2A \quad (1)$$

where A is the cross-sectional area of the film. In all of the present simulations, the cross-sectional area used was 30.76 nm^2 .

Work of adhesion

The work of adhesion of the epoxy-epoxy interface requires input from two MD simulations. The first one is that of the thin film (Figure 2(b)), and the second one is the simulation of the epoxy with an interface included (Figure 3). As discussed previously, the simulation models are constructed such that two epoxy-epoxy interfaces exist (Figure 3). The work of adhesion W is therefore

$$W = (E_{film,A} + E_{film,B} - E_{epoxyandinterface}) / 4A \quad (2)$$

where $E_{epoxyandinterface}$ is the total potential energy of the epoxy with interface simulation, and A and B refer to the two films. Here Eq. (2) has been updated from previous work [1] to account for the two interfaces. In this case, it is assumed that $E_{film,A} = E_{film,B}$. Two epoxy-epoxy interface simulations were carried out starting from different initial configurations (described earlier).

Work of adhesion with water

While it is understood that the work of adhesion in liquids is different from that of dry interfaces [13], a method to account for how it is different is required. It is proposed here that the total energy of the epoxy-epoxy interface with water simulation includes the water-water and water-epoxy interactions, and that these

interactions must be included in the calculation to obtain the work of adhesion in the presence of water. Therefore the work of adhesion in the presence of water is

$$W = (E_{film,A} + E_{film,B} + E_{water-water} + E_{water-epoxy} - E_{epoxyandinterface,water}) / 4A \quad (3)$$

The total potential energy of the epoxy-epoxy simulation with water at the interface (Figure 4) is $E_{epoxyandinterface,water}$. The energy of the water-water interaction $E_{water-water}$ is calculated as the total non-bonded water-water interaction from the Lennard-Jones and Coulombic contributions. The energy of the water-epoxy interaction $E_{water-epoxy}$ includes the non-bonded interaction between the epoxy and the water and is also calculated from the Lennard-Jones and Coulombic contributions. Altogether 6 simulations (described earlier) were performed for the water molecules starting in different initial configurations at the interface.

RESULTS AND DISCUSSION

The surface energy calculated by using Eq (1), and the contributing potential energies of the bulk and thin film epoxy simulations are reported in Table 1. The potential energies are averaged every 50 steps over 50,000 steps at 1 fs per time step. The surface energy of the epoxy from Eq(1) agrees within 9% with an experimental value for an amine cured epoxy[13].

The work of adhesion for the epoxy-epoxy interface calculated by using Eq. (2) and the contributing potential energies of the epoxy with interface simulations and the epoxy thin film are also reported in Table I. The potential energies of the epoxy with interface simulations were only 67 kJ/mol apart demonstrating good repeatability. Half of this range is reported as the uncertainty in Table I. The resulting work of adhesion is within the range reported experimentally in the literature (Table I). The first range of values between 88-99 mJ/m² is for epoxy/carbon fiber reinforced plastics (CFRP), and the second range of 50-90 mJ/m² is for epoxy against other polymer surfaces [13]. The CFRP surfaces are

TABLE I. SIMULATION DATA AND RESULTS

Simulation (Number of Configurations)	Energy (kJ/mol)	Surface Energy (mJ/m²)	Work of Adhesion (mJ/m²)	Surface Energy (mJ/m²) Ref.[13]	Work of Adhesion (mJ/m²) Ref.[13]
Bulk Epoxy	82300				
Thin Film Epoxy	83800	42		46.2	
Epoxy with interface (2)	162220±30		73.2±0.4		50-90 or 88-99
Epoxy with interface and water (6)	154000±1200		62±16		22-44
Water-water and water-epoxy interaction (6)	-9100 ±200				

likely to be resin rich with some contribution from the carbon fiber, and the other surfaces provide a more general comparison with other polymeric materials.

The magnitude of the work of adhesion at the epoxy-epoxy interface with water is reported in Table I, along with the total potential energies of the epoxy-epoxy simulation with water at the interface and the contribution of the combined water-water and water-epoxy energies. A density profile of the epoxy and the water as a function of the z-dimension of the simulation is plotted in Figure 4(c) for one of the simulations of the epoxy-epoxy interface with water. In these simulations, the water is mostly located at the interfaces with some diffusion into the epoxy. The magnitude of the work of adhesion from the simulations is reduced by 15% for the

epoxy interface with 1.6 wt% water relative to the interface with no water. Also in Table I, the uncertainties provided for the water simulations are standard deviations in the quantities utilizing results from different initial configurations of each of the 6 simulations. The amount of variation in work of adhesion at 1.6 wt% water is 26%. Compared to the experimental range of the epoxy/CFRP system reported in Table I, the simulations agree that there is a reduction in magnitude, and demonstrate that a range of work of adhesion values is available resulting from different water configurations at the interface. Neither the amount of water present nor the test method used is given in Ref. [13].

CONCLUDING REMARKS

Molecular dynamics simulations of an amine cured epoxy were performed. The surface energy of the epoxy and the work of adhesion at the epoxy-epoxy interface with and without water were calculated. A previously developed theory for calculating the work of adhesion at polymer interfaces was modified to account for two epoxy-epoxy interfaces. Further modification was done to account for the presence of water at the interface. By optimizing the force field, a surface energy within 9% of the experimental value for an amine cured epoxy is obtained. The computed work of adhesion for the epoxy-epoxy interface is also within the experimental range. The completed work of adhesion for the interface with water demonstrated a similar trend as observed from experiment. The simulations demonstrated that adding water at the interface reduces the magnitude of the work of adhesion, and that a range of values can be found. Therefore, the simulation methods that are applied and developed in this work are expected to be applicable for other epoxy adhesives and to determine the effects of moisture uptake on their work of adhesion.

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